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No. 10/736,921
60246-220; 10691**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicant: Wei
Serial No.: 10/736,921
Filed: December 16, 2003
Group Art Unit: 1753
Examiner: Mayekar, Kishor
Title: MULTI-LAYERED PHOTOCATALYST/THERMOCATALYST
FOR IMPROVING INDOOR AIR QUALITY

Commissioner for Patents
P.O. Box 1450
Alexandria VA 22313-1450

REPLY BRIEF

Dear Sir:

The following remarks are in reply to the Examiner's answer dated 20 December 2007. The Appeal Brief fee has already been paid. Any additional fees or credit may be charged to Deposit Account No. 030835 in the name of Carrier Corporation.

REMARKS

Respectfully, the Examiner's Answer raises numerous additional issues that require a brief response as follows.

Applicant acknowledges and appreciates withdrawal of the rejection of claims 1-21, 28-30, 34, 36, and 37 under 35 U.S.C. §112, first paragraph.

Regarding Appellants argument under section III of the Appeal Brief, the Examiner additionally brings up whether the specific citations to the specification support the claimed subject matter. Respectfully, the cited paragraphs of the specification illustrate the capability of the inner layer to react with carbon oxide compounds. That is, the inner layer may react with carbon monoxide and carbon dioxide, which is a product of reaction from the intermediate layer. As further support, Appellant also submits an article "Carbon Dioxide and Carbon Monoxide Hydrogenation over Gold Supported on Titanium, Iron, and Zinc Oxides" by Sakurai et. al. The

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Sakurai article discloses a catalyst that includes gold deposited on titanium dioxide. One example of Appellant's inner layer includes nano-dispersed gold on titanium dioxide. The first sentence of the abstract of the Sakurai article discloses that gold deposited on titanium dioxide is reactive with both carbon dioxide and carbon monoxide. Therefore, one of ordinary skill would understand from the specification of the present application that the inner layer may be reactive with carbon oxides such as carbon monoxide and carbon dioxide.

Regarding Appellant's argument under section IV of the Appeal Brief, the Examiner responds that there is proper motivation for making the proposed combination. Respectfully, Appellant disagrees because the given reason that the combination would "result in the application of Kobayashi's photocatalytic metal to a photocatalytic fluid purification system" is clearly hindsight reasoning. The rejection merely states what the result of the combination would be and does not provide any reasoning of why one of ordinary skill would be led to combine the references as proposed or whether one would expect any improvement from the combination.


Regarding Appellant's argument for claim 27 under section V of the Appeal Brief, the Examiner responds that the requisite motivation has been provided. Respectfully, Appellant disagrees because the rejection does not even mention all the claimed elements. For instance, claim 27 recites the locations of the substrates relative to an inlet of the purification system. Therefore, the required reasoning is not present because the rejection does not appear to consider an inlet or provide any reasoning related to arranging substrates relative to an inlet.

CLOSING

For all the reasons set forth above, and the reasons set forth in Appellant's Appeal Brief, the rejections of the claims is improper and should be reversed.

Respectfully Submitted,

CARLSON, GASKEY & OLDS, P.C.

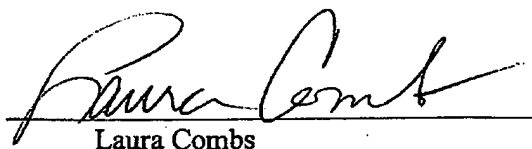

Matthew L. Koziarz, Reg. No. 53,154
400 West Maple Road, Suite 350
Birmingham, Michigan 48009
(248) 988-8360

Dated: February __, 2008

Serial No. 10/736,921
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CERTIFICATE OF TRANSMISSION UNDER 37 CFR 1.8

I hereby certify that this correspondence is being facsimile transmitted to the United States Patent and Trademark Office, fax number (571) 273-8300, on February 18, 2008.


Laura Combs



Applied Catalysis A: General 127 (1995) 93–105



Carbon dioxide and carbon monoxide hydrogenation over gold supported on titanium, iron, and zinc oxides

Hiroaki Sakurai *, Masatake Haruta

Osaka National Research Institute, AIST, 1-8-31 Midorigaoka, Ikeda, 563, Japan

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Abstract

Gold deposited on TiO_2 , Fe_2O_3 , ZnO and ZnFe_2O_4 with high dispersion was found to be active for the hydrogenation of both carbon dioxide and carbon monoxide at temperatures between 150 and 400°C. Over the above catalysts, methanol was produced more readily from carbon dioxide than from carbon monoxide. In particular, Au/ZnO and $\text{Au/ZnFe}_2\text{O}_4$ showed high methanol selectivities from carbon dioxide, which were comparable to those obtained for copper catalysts. As for methanol synthesis from carbon monoxide, only Au/ZnO gave appreciable yields with similar selectivity as copper catalysts. The comparison between experimental and thermodynamic data proved that over all the catalysts except for Au/TiO_2 three reactions, namely between carbon dioxide and methanol, carbon monoxide and methanol, carbon dioxide and carbon monoxide, simultaneously reached equilibria at temperatures above 300°C and that the methanol yield decreased with further increase in temperature. Hydrocarbons were formed at high temperatures and the resulting water was also involved in the above equilibria. As a main hydrocarbon product, methane was obtained much more selectively from carbon dioxide than from carbon monoxide. Ethane and propane were also produced from carbon dioxide and carbon monoxide over gold supported on reduced iron oxides.

Keywords: Carbon dioxide; Carbon monoxide; Gold catalysts; Hydrogenation; Methanol synthesis

1. Introduction

Methanol is commercially produced from mixtures of carbon monoxide and hydrogen containing small amounts of carbon dioxide [1]. The growing concern on the green-house effect caused by carbon dioxide has motivated laboratory-scale studies of methanol synthesis by the hydrogenation of pure carbon dioxide [2–5].

* Corresponding author. Tel. (+81-727) 519656, fax. (+81-727) 519630.

For methanol synthesis from both carbon monoxide and carbon dioxide, copper based catalysts, such as Cu/ZnO/Al₂O₃ and Cu/ZnO/Cr₂O₃, have been most widely used and they are recognized to be more active than supported precious metal catalysts [6–9].

Frost [10] proposed the simple hypothesis that catalytic activity for methanol synthesis was essentially determined by the concentration of oxygen vacancies on the oxide surface around the perimeter of metal particles. The role of deposited metals was assumed to be to change the concentration of such vacancies through the formation of a Schottky junction. This interpretation could lead to the prediction that gold and silver should also exhibit catalytic activity for methanol synthesis. Although a few subsequent papers reported by other workers described that silver [11,12] and gold [13,14] showed no detectable methanol synthesis activities from carbon monoxide, the recent paper by Baiker et al. [15] has clearly demonstrated that all IB metals (Cu, Ag and Au) supported on ZrO₂ are catalytically active for methanol synthesis from carbon dioxide. We have also reported that carbon dioxide hydrogenation over gold supported on several kinds of metal oxides can take place and that product selectivity appreciably changes depending on the nature of the support oxides [16].

Since gold is catalytically the least active of the IB metals, the genesis of a substantial catalytic activity by combining gold with suitable metal oxide supports should help elucidate the general mechanism for methanol synthesis and develop new innovative catalysts. The present study deals with some typical gold catalysts supported on titanium-, iron-, and zinc-based oxides to compare methanol formation and the distribution of other products in the hydrogenation of carbon dioxide and carbon monoxide.

2. Experimental

Three gold catalysts, Au/ZnO, Au/Fe₂O₃, and Au/ZnFe₂O₄, were prepared by a coprecipitation method from the mixed aqueous solution of chloroauric acid and metal nitrates according to the procedure described elsewhere [17–19]. The gold loading was adjusted to 5 atom-% [$= 100\text{Au}/(\text{Au} + \text{Metal})$] in the starting solutions. For the preparation of Au/TiO₂, JRC-TiO₂ (reference catalyst of the Catalysis Society of Japan) was used as a support. On the TiO₂ powder, Au (2 atom-%) was deposited by a deposition-precipitation method [19,20]. For comparison, Cu/ZnO (Cu 5 atom-%) was also prepared by coprecipitation from the nitrates of copper and zinc, and Au/ZnO (Au 5 atom-%) by impregnation of ZnO with chloroauric acid. The catalyst precursors were finally calcined in air at 400°C for 4 h. Commercial copper catalyst Cu/ZnO/Al₂O₃ (MDC-3, Catalysts and Chemicals Inc., Far East), was also used for the comparison. The composition of the catalyst was measured by X-ray fluorescence (XRF), and found to be Cu:Zn:Al = 42:45:13 in atomic ratio.

The specific surface areas of the catalysts were measured by a BET single point method by using a Quantasorb Jr. analyzer. X-ray diffraction of each sample was obtained using a Rigaku X-ray powder diffractometer. The crystallite sizes of gold for the precipitated samples were calculated from peak half-widths of Au(111) by using Scherrer's equation.

Catalytic activity measurements were carried out by using a fixed-bed continuous flow reactor. After introducing pretreatment gas (1% H₂ balanced with N₂) at 250°C for 8–12 h, the reactant gas was passed through the catalyst bed (1 g, 12–42 mesh) under a total pressure of 50 atm and at a space velocity of 3000 h⁻¹ ml/g_{catal.} at temperatures of 150, 200, 250, 300, 350 and 400°C. The compositions of the reactant gases used were CO₂/H₂/Ar=23/67/10 for carbon dioxide hydrogenation and CO/H₂/Ar=30/60/10 for carbon monoxide hydrogenation. The detailed reaction procedure and the method for product gas analysis by gas chromatography (GC) are given in the previous paper [16].

3. Results

3.1. Reactivity of carbon dioxide and carbon monoxide

Table 1 shows the results of carbon dioxide hydrogenation together with the data for the physical properties of the prepared catalysts. The specific surface area of the catalysts ranged from 30 to 60 m² g⁻¹. The crystallite size of gold before reaction was less than 4 nm except for the impregnated Au/ZnO.

Over the gold catalysts prepared by coprecipitation and deposition-precipitation, carbon dioxide conversion at 250°C was notably different (4–19%) depending on the oxidic support material. Both Au/Fe₂O₃ and Au/TiO₂ showed almost the same carbon dioxide conversion as the copper catalysts did. Zinc-containing catalysts, Au/ZnO and Au/ZnFe₂O₄, showed high methanol selectivities of over 45%. The conversion increased with increasing temperature and reached a value between 35 and 40% at 400°C. At such a high temperature, methanol production was very low and the main product was carbon monoxide over Au/ZnO, Cu/ZnO and Cu/ZnO/Al₂O₃, whereas relatively large amounts of hydrocarbons were produced over the other catalysts. The Au/ZnO catalyst prepared by the impregnation method had low activity, resulting in a conversion less than 4% even at 400°C.

In carbon dioxide hydrogenation at a fixed temperature of 250°C, Au/Fe₂O₃ was chemically stable and gave an almost constant level of carbon dioxide conversion exceeding 17% with a methanol yield over 5% for 5 h. However, after the catalyst temperature had been raised once up to 400°C, the catalytic activity was significantly changed in the second reaction cycle. The overall carbon dioxide conversion and methanol yield at 250°C decreased to a level of about 70% of the initial values in the first reaction cycle.

Table 1
Activity of gold catalysts for carbon dioxide hydrogenation^a

Catalysts	d_{Au}^b (nm)	S.A. ^c (m ² g ⁻¹)	Temp. (°C)	CO ₂ conv. (%)	Product selectivities				
					MeOH (%)	CO (%)	CH ₄ (%)	C ₂ (%)	C ₃ (%)
Au/ZnO	3.5	41.0	250	8.2	48.8	51.2	0.0	0.0	0.0
			300	24.5	21.2	78.8	0.0	0.0	0.0
			400	37.7	1.1	98.4	0.5	0.1	0.0
Au/ZnO ^d	33.9	—	250	0.0	—	—	—	—	—
			300	0.2	100.0	0.0	0.0	0.0	0.0
			400	3.7	32.4	56.8	5.4	0.0	0.0
Au/Fe ₂ O ₃	3.3	32.8	250	18.4	29.3	69.6	1.1	0.0	0.0
			300	25.3	14.2	78.3	7.5	0.0	0.0
			400	38.3	0.8	67.1	32.4	0.5	0.0
Au/Fe ₂ O ₃ ^e	—	—	250	12.4	31.5	68.5	0.0	0.0	0.0
			300	24.3	13.6	77.8	8.2	0.4	0.0
			400	40.0	0.0	40.5	38.5	11.8	9.3
Au/TiO ₂	3–4 ^f	41.0	250	18.6	6.5	75.3	18.3	0.0	0.0
			300	25.6	1.2	58.6	39.8	0.0	0.0
			400	38.0	0.3	47.6	52.4	0.0	0.0
Au/ZnFe ₂ O ₄	2.8	54.7	250	4.2	64.3	35.7	0.0	0.0	0.0
			300	20.1	24.4	74.6	1.0	0.0	0.0
			400	34.7	0.0	40.6	28.8	13.0	17.9
Cu/ZnO	—	49.1	250	17.2	37.2	62.8	0.0	0.0	0.0
			300	25.3	16.6	83.0	0.01	0.0	0.0
			400	39.0	1.3	97.9	0.8	0.3	0.1
Cu/ZnO/Al ₂ O ₃ ^g	—	54.2	250	22.8	51.3	48.7	0.0	0.0	0.0
			300	26.6	17.3	82.7	0.4	0.0	0.0
			400	38.1	1.3	94.2	3.4	1.0	0.5

^a Reaction conditions: CO₂/H₂/Ar = 23/67/10, total pressure = 50 atm, SV = 3000 h⁻¹ ml/g_{cat}.

^b Crystallite size of gold calculated by using Scherrer's equation.

^c BET surface area of catalyst.

^d Prepared by impregnation method.

^e Result of the second reaction cycle repeated after the final reaction at 400°C in the first cycle.

^f Mean particle diameter of gold obtained from TEM photographs (observed in a different sample prepared under the same conditions).

^g Commercial catalyst supplied by Catalysts & Chemicals Inc., Far East.

The results of carbon monoxide hydrogenation are shown in Table 2. At 250°C methanol was the main product over ZnO containing catalyst, i.e. Au/ZnO, Cu/ZnO and Cu/ZnO/Al₂O₃, with selectivities of more than 70%. At a temperature as high as 400°C, large amounts of carbon dioxide were produced together with hydrocarbon formation, especially with high carbon monoxide conversion over Au/Fe₂O₃ and Au/TiO₂.

3.2. Methanol production

In the hydrogenation of both carbon dioxide and carbon monoxide, the curves for the temperature dependency of methanol yield are not monotonously rising but

Table 2
Activity of gold catalysts for carbon monoxide hydrogenation^a

Catalysts	d_{Au}^b (nm)	S.A. ^c (m ² g ⁻¹)	Temp. (°C)	CO conv. (%)	Product selectivities				
					MeOH (%)	CO ₂ (%)	CH ₄ (%)	C ₂ (%)	C ₃ (%)
Au/ZnO	3.5	41.0	250	3.7	70.3	29.7	0.3	0.0	0.0
			300	9.3	81.7	10.8	4.3	0.2	0.0
			400	17.5	4.0	47.4	42.3	3.4	1.1
Au/Fe ₂ O ₃	3.3	32.8	250	9.8	16.3	54.1	13.3	9.2	8.2
			300	79.6	2.5	54.4	20.7	10.7	11.6
			400	88.8	0.1	52.0	18.7	13.5	15.7
Au/TiO ₂	—	41.0	250	17.2	0.6	52.3	40.7	5.2	0.6
			300	65.3	0.2	53.3	34.5	9.3	2.8
			400	88.4	0.0	46.9	38.9	11.9	2.3
Cu/ZnO	—	49.1	250	2.5	72.0	24.0	0.8	0.4	0.0
			300	10.3	81.6	11.7	3.9	1.9	1.0
			400	17.5	4.0	47.4	38.3	7.4	2.3
Cu/ZnO/Al ₂ O ₃	—	54.2	250	28.5	89.5	8.1	0.4	0.4	0.4
			300	26.0	45.3	36.5	3.1	5.4	9.2
			400	26.3	2.7	49.8	30.8	10.3	6.1

^a Reaction conditions: CO/H₂/Ar = 30/60/10, total pressure = 50 atm, SV = 3000 h⁻¹ ml/g_{cat}.

^b Crystallite size of gold calculated by using Scherrer's equation.

^c BET surface area of catalyst.

^d Commercial catalyst supplied by Catalysts & Chemicals Inc., Far East.

parabolic as we reported earlier [16], giving maxima at temperatures between 250 and 300°C. Figs. 1 and 2 show the relationship between methanol selectivities and yields in carbon dioxide and carbon monoxide hydrogenation, respectively.

The maximum methanol yields from carbon dioxide over Au/ZnO, Au/Fe₂O₃ and Au/ZnFe₂O₄ were comparable to that over Cu/ZnO with the same metal

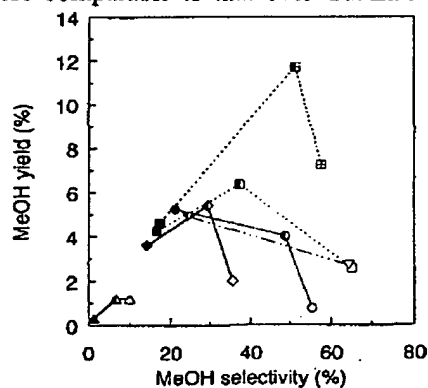


Fig. 1. Methanol yield in carbon dioxide hydrogenation as a function of methanol selectivity: (O) Au/ZnO; (□) Cu/ZnO; (◇) Au/Fe₂O₃; (Δ) Au/TiO₂; (▽) Au/ZnFe₂O₄; (B) Cu/ZnO/Al₂O₃. Filled symbols indicate the reaction at 200°C; half filled symbols indicate the reaction at 250°C; open symbols indicate the reaction at 300°C.

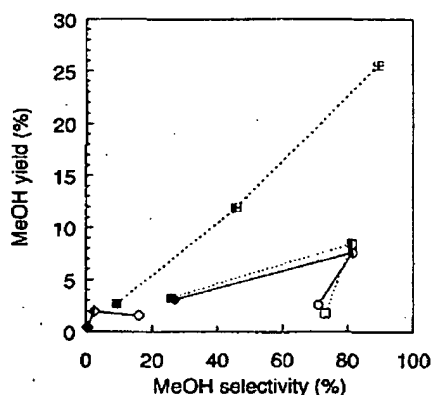


Fig. 2. Methanol yield in carbon monoxide hydrogenation as a function of methanol selectivity: (O) Au/ZnO; (□) Cu/ZnO; (◇) Au/Fe₂O₃; (⊞) Cu/ZnO/Al₂O₃. Filled symbols indicate the reaction at 250°C; half filled symbols indicate the reaction at 300°C; open symbols indicate the reaction at 350°C.

loading, as we reported earlier [16], although less than half of the maximum yield over the commercial Cu/ZnO/Al₂O₃ catalyst. Au/TiO₂ gave low but significant methanol yields of over 1%. With respect to methanol selectivities, both Au/ZnO and Au/ZnFe₂O₄ were superior to the other gold catalysts, and comparable to copper catalysts.

For carbon monoxide hydrogenation, Cu/ZnO and Au/ZnO showed almost similar activities, which were much lower than that of the commercial Cu/ZnO/Al₂O₃ catalyst. The maximum methanol yield over Au/Fe₂O₃ was less than one third of that for Au/ZnO. Methanol production over Au/TiO₂ was hardly observed, with a yield less than 0.1%. In the comparison of maximum methanol yields from carbon dioxide and carbon monoxide, carbon monoxide gave higher methanol yields over Au/ZnO and Cu/ZnO and the reverse over Au/Fe₂O₃ and Au/TiO₂. At lower temperatures, e.g. at 200°C, all catalysts except Au/ZnFe₂O₄ gave detectable methanol yields in carbon dioxide hydrogenation, but negligible yields in carbon monoxide hydrogenation. The methanol selectivities for carbon monoxide hydrogenation over Au/ZnO and Cu/ZnO were similar and much higher than those for carbon dioxide hydrogenation. On the other hand, the methanol selectivities in carbon monoxide hydrogenation over Au/Fe₂O₃ and Au/TiO₂ were lower than those in carbon dioxide hydrogenation.

3.3. Formation of hydrocarbons

Methane was the major hydrocarbon by-product in carbon dioxide hydrogenation over Cu/ZnO, Au/ZnO, Au/Fe₂O₃ and Au/TiO₂, with only small amounts of higher hydrocarbons being produced (Table 1). In the case of Au/ZnFe₂O₄, ethane and propane were also formed at 400°C and a similar product distribution was observed over Au/Fe₂O₃ in the second reaction. However, the formation of olefinic hydrocarbons was not observed.

Table 3
Changes of the Au/Fe₂O₃ catalyst during pretreatment and carbon dioxide hydrogenation^a

Procedure	d_{Au}^b (nm)	Oxide phase of iron oxide ^c	MeOH yield (%)	Generated hydrocarbons ^d
Calcination in air at 400°C	3.3	α -Fe ₂ O ₃	—	—
H ₂ reduction at 250°C	3.5	Fe ₃ O ₄	—	—
Reaction at 250°C in the first cycle	3.5	Fe ₃ O ₄	5.4	none
Reaction at 400°C in the first cycle	*	*	0.3	CH ₄
Reaction at 250°C in the second cycle	*	*	3.9	none
Reaction at 400°C in the second cycle	6.3	Fe ₃ O ₄	0.0	CH ₄ , C ₂ H ₆ , C ₃ H ₈

^a Reaction conditions: CO/H₂/Ar = 30/60/10, total pressure = 50 atm, SV = 3000 h⁻¹ ml/g_{cat}. After hydrogen reduction at 250°C, reaction was carried out from 150 to 400°C in 50°C steps as the first cycle, and then repeated from 150°C as the second cycle.

^b Crystallite size of gold calculated by using Scherrer's equation from XRD data after each procedure.

^c Detected phase of oxide in XRD analysis after each procedure.

^d Main hydrocarbons produced with yields exceeding 0.5%.

* Not measured.

The change of the Au/Fe₂O₃ catalyst during pretreatment and the carbon dioxide hydrogenation reaction was investigated by X-ray diffraction (XRD) measurements (Table 3) during the first and the second reaction cycle. Fresh Au/Fe₂O₃ after calcination in air at 400°C was composed of gold particles with an average crystallite size of 3.3 nm and an α -Fe₂O₃ oxide phase. After hydrogen pretreatment, iron oxide was reduced to Fe₃O₄ with a slight increase in gold particle size to 3.5 nm. This particle size was maintained during the reaction at 250°C in the first cycle. After reaction at 400°C in the second cycle the catalyst was further changed because of the much more severe reducing conditions. The particle size of gold increased to 6.3 nm, which might be the cause of the decrease in methanol yield in the second reaction cycle. The formation of C₂ and C₃ hydrocarbons in the second cycle can be ascribed to the deeply reduced Fe₃O₄ surface.

In the case of Au/ZnFe₂O₄, a separate ZnO phase, which was not seen before reaction, was detected by XRD after reaction as well as the reduction of iron species. The formation of C₂ and C₃ observed can also be ascribed to the reduced oxide surface.

The results of carbon monoxide hydrogenation (Table 2) show that methane, ethane and propane were formed at 400°C over all the catalysts. Even over Au/ZnO and Cu/ZnO, an appreciable amount of methane was formed with a selectivity higher than 38%. Very small amounts of ethene and propene were detected over Au/Fe₂O₃. When C₂ and C₃ hydrocarbons were formed, the distributions of hydrocarbons were found to be almost identical with the Schulz–Flory distribution.

3.4. Thermodynamic equilibrium

At higher temperatures, methanol yields from both carbon dioxide and carbon monoxide decreased with increasing temperature over all catalysts. This tendency

can be explained by thermodynamic equilibria of related reactions. The equilibria which are involved in carbon dioxide hydrogenation are



and the corresponding equilibrium equations are

$$K_1 = \frac{[\text{CH}_3\text{OH}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]^3} \cdot \frac{1}{P^2} \quad (5)$$

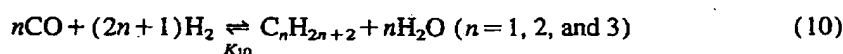
$$K_2 = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]} \quad (6)$$

$$K_3 = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} \cdot \frac{1}{P^2} \quad (7)$$

$$K_4 = \frac{[\text{CH}_4][\text{H}_2\text{O}]^2}{[\text{CO}_2][\text{H}_2]^4} \cdot \frac{1}{P^2} \quad (5)$$

where P (=45 atm) is the total pressure of the reaction mixture excluding the partial pressure of the inert gas (Ar).

Similarly, for carbon monoxide hydrogenation, the following reactions and equations should be taken into account.



$$K_9 = \frac{1}{K_2} = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} \quad (11)$$

$$K_{10} = \frac{[\text{C}_n\text{H}_{2n+2}][\text{H}_2\text{O}]^n}{[\text{CO}]^n[\text{H}_2]^{2n+1}} \cdot \frac{1}{P^{2n}} \quad (12)$$

For carbon dioxide hydrogenation, the concentrations of CO_2 , H_2 and H_2O were calculated from the analytical data of methanol, carbon monoxide and methane

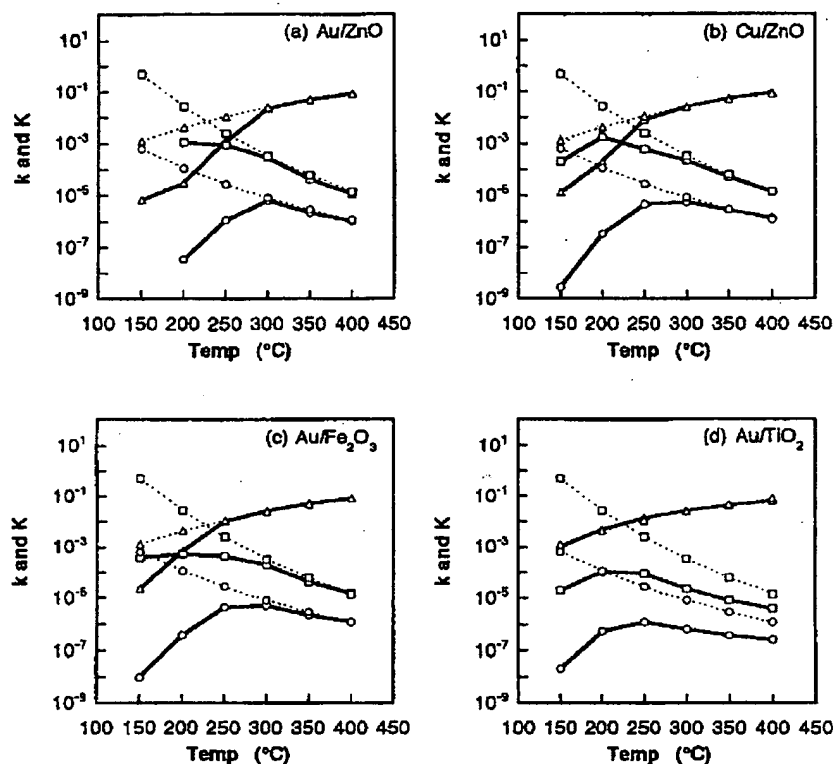


Fig. 3. Experimental and equilibrium constants in carbon dioxide hydrogenation as a function of reaction temperature. (O) $\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$; (Δ) $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$; (\square) $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$; (solid lines) k calculated from experimental data; (broken lines) K in equilibrium.

using the material balance equations, as already reported in the preceding paper [16]. Also for carbon monoxide hydrogenation, the concentrations of CO, H_2 and H_2O were calculated from the analytical data of CH_3OH , CO_2 , CH_4 , C_2H_6 and C_3H_8 . These values are substituted for the right hand terms of Eqs. (5)–(8) and (11), (12). The resulting values corresponding to the equilibrium constants K_1 – K_4 , K_9 and K_{10} are referred to as k_1 – k_4 , k_9 and k_{10} .

Fig. 3 shows the results of carbon dioxide hydrogenation over Au/ZnO, Cu/ZnO, Au/ Fe_2O_3 and Au/ TiO_2 . Because methane formation (k_4) is far from the equilibrium value (K_4) over the full temperature range, the plots for k_4 and K_4 were omitted. This figure clearly shows that methanol production from carbon dioxide [Eq. (1)] over Au/ZnO, Cu/ZnO and Au/ Fe_2O_3 decreased with increasing temperature due to thermodynamic limitations at temperatures above 300°C, where carbon monoxide production by the reverse water-gas shift reaction [Eq. (2)] increased with increasing temperature owing to the equilibrium. Under such a condition, methanol production/decomposition reaction from/to carbon monoxide [Eq. (3)] should also be in equilibrium, and k_1 , k_2 and k_3 coincide with K_1 , K_2 and

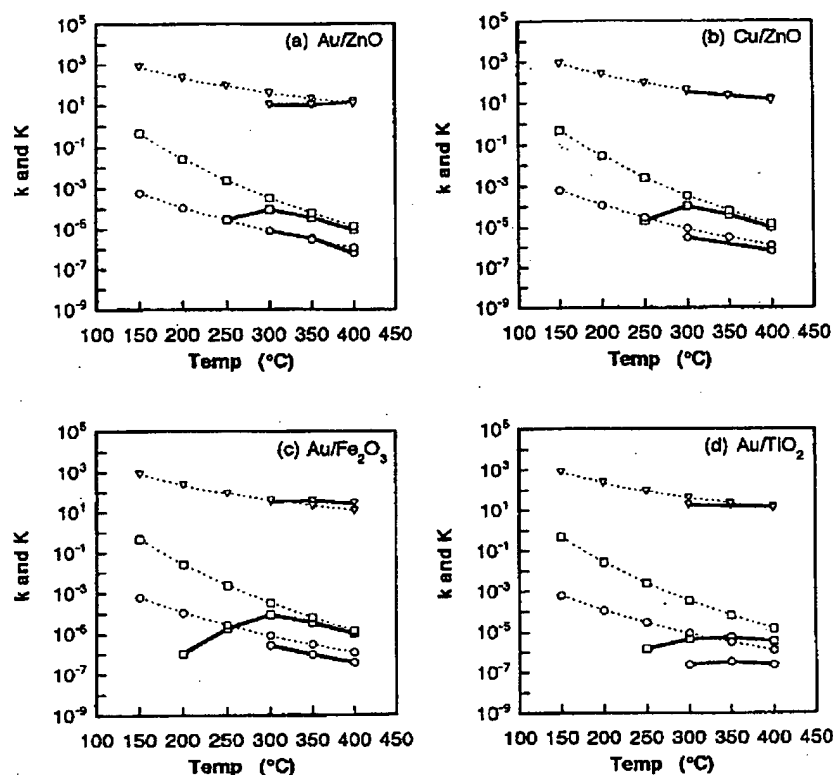


Fig. 4. Experimental and equilibrium constants in carbon monoxide hydrogenation as a function of reaction temperature. (○) $\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$; (▽) $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$; (□) $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$; (solid lines) k calculated from experimental data; (broken lines) K in equilibrium.

K_3 , respectively. In the case of Au/TiO_2 , the methanol yield did not reach equilibrium at temperatures up to 400°C and the decrease of methanol yield over 250°C should be ascribed to other reasons. Another point to note for Au/TiO_2 is the very high activity for the reverse water-gas shift reaction. Fig. 3d shows that this reaction has already reached equilibrium at a temperature as low as 150°C .

Fig. 4 shows the results of carbon monoxide hydrogenation over the same catalysts as shown in Fig. 3. Hydrocarbon formation, Eq. (6), is far from equilibrium and therefore omitted from the figure. The k_1 and k_9 values below 300°C are not shown here, because the amount of water is not directly analyzed by GC and it is difficult to calculate such a small amount of water only from the material balance. The figure shows the methanol production from carbon monoxide (k_3), water-gas shift reaction (k_9), and the relationship between carbon dioxide and methanol (k_1) coincide with the equilibrium values at temperatures above 300°C except for the case of Au/TiO_2 . Both k_1 and k_3 were less than the equilibrium value K_1 and K_3 over Au/TiO_2 even at 400°C , which was also observed in Fig. 3d.

4. Discussion

Although it was previously reported by other workers that Au/TiO₂ [13] and Au/CeO₂ [14] were poorly active for carbon monoxide hydrogenation, the above experimental results have clearly shown that some supported gold catalysts exhibit appreciable activity for methanol synthesis from both carbon monoxide and carbon dioxide. Such a pronounced discrepancy from the previously reported work can be attributed to the difference in the preparation methods of the catalysts. The particle diameter of gold in Au/ZnO prepared by impregnation (Table 1), 34 nm, indicates that impregnation of HAuCl₄ [13] and the oxidation of gold alloys [14] could not give rise to the high dispersion of gold. Coprecipitation and deposition–precipitation are advantageous as compared to impregnation for the following reasons [19].

- (1) Gold particles are very small, generally with a diameter smaller than 4 nm and uniformly dispersed onto the support oxide.
- (2) Gold particles, hemispherical in shape, are firmly attached to the oxide surface.
- (3) The concentration of residual chloride anion can be minimized by repetitive washing before calcination.

In fact, Au/ThO₂ [10] and Au/ZrO₂ [15] prepared by coprecipitation have also been reported to be active for methanol production from carbon monoxide and carbon dioxide, respectively.

Of the gold catalysts, only ZnO-containing catalysts gave methanol in high selectivities. Further, Au/ZnO showed comparable methanol yield and selectivities to Cu/ZnO which has the same metal loading. This suggests that the combination of a IB metal and a ZnO support is essentially effective for methanol synthesis. The lower activity of Au/ZnO than commercial copper catalysts may be largely due to the smaller metal loading.

It should be noticed that carbon dioxide can be hydrogenated at lower temperatures than carbon monoxide over all the catalysts tested, which suggests that methanol can be directly formed from carbon dioxide at least in the lower temperature range. Methanol formation from carbon dioxide is always accompanied by carbon monoxide production. However, recent mechanistic studies of carbon dioxide hydrogenation over copper catalysts indicate that carbon dioxide is the main carbon source of methanol even from a carbon dioxide and carbon monoxide mixture [21,22].

As widely accepted for copper-based catalysts [23], carbon dioxide may adsorb as carbonate over gold catalysts too. This adsorbed carbonate is hydrogenated to formate and methoxy species and finally desorbs as methanol [16], while C-bonded intermediates, such as formyl and hydroxymethylene, may be responsible for methanol formation from carbon monoxide.

Concerning hydrocarbon formation, only methane was observed for carbon dioxide hydrogenation over Au/ZnO and Au/TiO₂, while methane, ethane, and propane were formed by carbon monoxide hydrogenation. The above difference in hydrocarbon distribution from carbon dioxide and carbon monoxide can be expected, if

hydrocarbon formation proceeds via intermediates similar to those observed in methanol formation, because carbon chains can easily grow via C-bonded intermediates. The hydrogenation of carbon dioxide was reported to give almost exclusively methane over other metal catalysts [24–27]. However, over Au/ZnFe₂O₄ and Au/Fe₂O₃ in the second reaction, ethane and propane are also formed even from carbon dioxide. The partial reduction of the oxide support can be assumed to enhance the formation of C-bonded intermediates from carbon monoxide molecules formed by the reverse water-gas shift reaction.

In carbon monoxide hydrogenation, if all carbon dioxide molecules are formed by the reaction of carbon monoxide with water [Eq. (9)] which is produced by the formation of hydrocarbons [Eq. (10)], the selectivity of carbon dioxide should coincide with the total selectivity of hydrocarbons. In fact, both selectivities of carbon dioxide and of total hydrocarbons were ca. 47% over Au/ZnO and Cu/ZnO at 400°C. In the case of Au/TiO₂, carbon dioxide selectivity (47%) is smaller than the selectivity of total hydrocarbons (53%), and the opposite over Au/Fe₂O₃ and Cu/ZnO/Al₂O₃. In particular, the carbon dioxide selectivity exceeded the total selectivity of hydrocarbons by 4% over Au/Fe₂O₃ (Table 2). Such an excess formation of carbon dioxide can be explained by the disproportionation of carbon monoxide:



where carbon may deposit on the catalyst surface. At 400°C, the molar ratio of total carbon to argon in outlet gas decreased to 70% of that in the inlet gas.

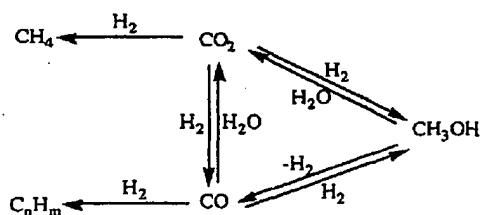
5. Conclusions

1. Gold supported on titanium, iron, zinc oxides exhibits an appreciably high activity for carbon dioxide and carbon monoxide hydrogenation, when very fine gold particles are deposited on oxide supports by either coprecipitation or deposition-precipitation methods.

2. Product selectivity is greatly affected by the support oxides. The combination of a IB metal and zinc containing oxide is effective for selective methanol synthesis. Au/Fe₂O₃ and Au/TiO₂ were more active for hydrocarbon formation and for both forward and reverse water-gas shift reactions.

3. Over all the catalysts tested, carbon dioxide produced methanol at lower temperatures, and produced methane more selectively than carbon monoxide.

4. The reaction paths for the reaction of carbon dioxide and carbon monoxide over supported gold catalysts can be summarized in the following scheme.



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